

# CATALYTIC REACTIONS IN WASTE PLASTICS AND COAL STUDIED BY HIGH PRESSURE THERMOGRAVIMETRY WITH ON-LINE GC/MS

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## INTRODUCTION

Waste plastics account for roughly 40% of landfill trash, of which only about 3% is recycled. The disposal of waste plastics is an important environmental problem. Clearly, the dominant components of waste plastics; mainly polyethylene, polystyrene, polypropylene are rich in carbon and hydrogen - the building blocks of petroleum, so that the possibility of converting waste plastic into liquid fuels is a productive alternative for plastic recycling. On the other hand, coal is hydrogen deficient, so co-processing of coal with waste plastics could be another way to recycle waste plastics into useful products.

Pyrolysis is a simple method to break the carbon-carbon bonds into relatively small molecular compounds by heating the polymers, but the major limitation of straight pyrolysis has been the poor selectivity for co-processing of coal and waste plastics. The use of various catalysts is a promising way of improving selectivity and yield. Catalytic liquefaction of coal has been widely studied<sup>1,2,3</sup>, but little is known about catalytic conversion of waste plastics and co-processing of coal with waste plastics<sup>4,5</sup>.

Development of efficient processes for converting solid waste materials and coal to useful products is often hindered by the lack of detailed fundamental data on real time thermal and catalytic reactions. A recently developed high pressure thermogravimetry (TG) system with on-line gas chromatography/mass spectrometry (GC/MS) modules provides detailed information on the pathways and mechanisms of the reactions which should benefit the screening of catalysts, help optimize reaction conditions, promote understanding of the function of the catalysts and provide a rapid and cost effective intermediate product analysis.

## EXPERIMENTAL

Experiments with commingled waste plastic in the presence of various catalysts and co-processing runs of coal and commingled waste plastic were performed in a high pressure TG/GC/MS system at 900 psi hydrogen or helium pressure. Details of the high pressure TG/GC/MS system have been described previously<sup>6</sup>. The commingled waste plastic analyzed was obtained by washing the colored plastic bottles and containers to remove contaminants and labels before sizing and shaving. Final size reduction was done by grinding in a k-TEC kitchen mill. The coal was Blind Canyon DECS-6 high volatile bituminous coal (-100 mesh) from the Penn State Coal Sample Bank. The characteristics of the commingled waste plastic and coal have been listed elsewhere<sup>7</sup>. The preparation of the superacid catalysts  $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ ,  $\text{ZrO}_2/\text{SO}_4^{2-}$  was described by Shabtai et al.<sup>7</sup>. The superacid catalysts  $\text{Al}_2\text{O}_3/\text{SO}_4^{2-}$ ,  $\text{Al}_2\text{O}_3/\text{SO}_4^{2-}$  (promoted by 0.5% Pt) were also prepared by Shabtai and co-workers, as will be described in this meeting<sup>8</sup>. The 25%  $\text{SiO}_2$ -75% $\text{Al}_2\text{O}_3$  catalyst was supplied by Gulf Research and Development Company and sized to 100-140 mesh. The catalyst Ni-Mo/ $\text{Al}_2\text{O}_3$ , provided by Engelhard Corporation was mixed with  $\text{SiO}_2\text{Al}_2\text{O}_3$  in a ratio of 4:1 (20-40 mesh size) and then sulfided.

## RESULTS AND DISCUSSION

A characteristic example of the type of analytical results obtainable with the system is shown in Figure 1. Hydropyrolysis of Blind Canyon DECS-6 coal was conducted at 900 psig  $\text{H}_2$  pressure while heating at 10 C/min up to 700 C. During this process three distinct stages can be distinguished from both the TG weight loss curve (Figure 1a) and the total ion chromatogram (Figure 1b), namely bitumen desorption, hydropyrolysis and hydrogasification. Product distributions are shown in Figure 2 by expanding the chromatograms to a single sampling interval. The first process stage (Figure 2a) occurs over the temperature range of 250-350 C with products consisting mainly of substituted two-ring aromatics and long chain alkanes from bitumen desorption due to the evaporation of unattached molecules<sup>9,10,11</sup>. The second stage spans the temperature range of 370-550 C. The products, primarily thought to be due to hydropyrolysis of the coal, include short chain aliphatics, substituted phenols and also long chain n-alkenes and -alkanes (Figure 2b)<sup>11,12</sup>. The compounds produced in the final hydrogasification stage (at temperatures above 550 C) are mainly non-substituted aromatics including benzene, naphthalene, anthracene/phenanthrene and four-ring aromatics and hydroaromatics (Figure 2c). By selecting a particular ion chromatogram over the entire reaction temperature range, it can be illustrated how the corresponding product is evolved during the reaction. Figure 3 illustrates evolution profiles of propyl phenol, anthracene/phenanthrene, and C5-substituted naphthalene. By looking at the

selective ion chromatograms, it is shown that phenol evolves during the second stage of the process, whereas nonsubstituted aromatics evolve mainly during the third stage, and substituted aromatics evolve during both first and second stages.

### Commingled Waste Plastics

Commingled waste plastic (about 35 mg) was subjected to three different temperature programs using a constant heating rate of 20 C/min up to 410 C, 420 C or 430 C separately, isothermal hold for 30 mins and then heating up to 700 C at 20 C/min to observe how decomposition reactions occur at a hydrogen pressure of 900 psig.

Figure 4 illustrates how temperature affects the decomposition reactions as measured by the weight loss as a function of temperature history and reaction time. At the end of the 30 min isothermal period at 410 C, weight loss of the waste plastic is approx. 17%, whereas at 430 C, approx. 84% of the weight is lost. These results illustrate that thermal decomposition reactions of waste plastic (in hydrogen) are strongly dependent on relatively small changes in reaction temperature. As indicated in our previous paper<sup>13</sup>, isothermal runs at relatively low temperatures are found to be effective in bringing out differences between catalytic and thermal processes. By contrast at a linear heating rate of 10 K/min, thermal reactions overwhelm the catalytic effect. An isothermal plateau at 420 C, producing approx. 54% weight loss within 30 min without catalyst, was selected to investigate catalytic effects by comparing the relative decomposition reaction rates, residual char amounts and time-resolved product evolution profiles of thermal and catalytic runs, respectively.

Experiments on the decomposition of commingled waste plastic in two different reactor gas atmospheres (helium and hydrogen) and with several different catalysts were performed at 900 psig using the temperature program mentioned above. Catalysts studied include solid superacids such as  $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ ,  $\text{Al}_2\text{O}_3/\text{SO}_4^{2-}$ ,  $\text{Al}_2\text{O}_3/\text{SO}_4^{2-}$  promoted by 0.5% Pt, and  $\text{ZrO}_2/\text{SO}_4^{2-}$  added at 10% to the feed, as well as conventional cracking catalyst,  $\text{SiO}_2/\text{Al}_2\text{O}_3$ , hydrocracking catalyst,  $\text{NiMo}/\text{Al}_2\text{O}_3$  mixed with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  in a 4:1 ratio (added at 50%) and HZSM-5 zeolite (added at 10%). Different shapes of the TG profiles (weight loss vs. reaction time) in Figure 5 indicate catalytic effects on reaction rates and residue formation during waste plastic decomposition reactions.

At 420 C, all catalysts tested increase decomposition reaction rates to a varying degree, as indicated by the slopes of the curves in Figure 5. At these high catalyst addition levels, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and HZSM-5 catalysts show the highest conversion rates. For the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  catalyst, measurable decomposition reactions occur at temperatures lower than 420 C. For the solid superacid catalysts studied, the approximate order of cracking activity is  $\text{ZrO}_2/\text{SO}_4^{2-} > \text{Al}_2\text{O}_3/\text{SO}_4^{2-} > \text{Pt}/\text{Al}_2\text{O}_3/\text{SO}_4^{2-} > \text{Fe}_2\text{O}_3/\text{SO}_4^{2-} > \text{no catalyst}$ . The weight loss after 30 min at 420°C is presented in Table 1 to illustrate how atmosphere and catalysts increase the yields of volatile products. In a hydrogen atmosphere the conversion yield is slightly increased compared to a helium atmosphere. Although  $\text{NiMo}/\text{Al}_2\text{O}_3$  mixed with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  catalyst is not as effective as  $\text{SiO}_2/\text{Al}_2\text{O}_3$  in cracking ability, it gives less residue formation due to the hydrogenation activity of the sulfided metal component. For catalysts such as  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ,  $\text{NiMo}/\text{Al}_2\text{O}_3$  mixed with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and HZSM-5, the decomposition reactions are completed at 420°C within 30 minutes. Therefore, no further reactions occur upon the increase of temperature.

The catalysts tested clearly improve the conversion rate of the commingled waste plastic, thereby lowering reaction temperature and/or shortening reaction time.

By examining the evolution profiles of volatile products by means of GC/MS changes in volatile product distributions as a function of reaction gas and catalysts can be measured. Several total ion chromatograms representing a single selected sampling period at different conditions are presented in Figure 6. The results show that thermal cracking, either in helium or hydrogen (only shown in hydrogen, Figure 6a) produced more evenly distributed long straight chain aliphatics including alkenes and alkanes (alkenes and alkanes are not separated by the 2 meter short GC column). With the catalysts, such as  $\text{Al}_2\text{O}_3/\text{SO}_4^{2-}$ ,  $\text{Pt}/\text{Al}_2\text{O}_3/\text{SO}_4^{2-}$ ,  $\text{ZrO}_2/\text{SO}_4^{2-}$ ,  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ,  $\text{NiMo}/\text{Al}_2\text{O}_3$ , mixed with  $\text{SiO}_2/\text{Al}_2\text{O}_3$ , more isomers of aliphatic products are produced (only shown with  $\text{ZrO}_2/\text{SO}_4^{2-}$ ; Figure 6c). The stronger the cracking catalysts, the lighter the aliphatics (only shown for  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ; Figure 6b). Strong cracking catalysts such as  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and HZSM-5 (zeolite) not only produce light aliphatics but also give high yields of substituted aromatics due to cyclization reactions promoted by acid catalysts as indicated in Figure 6d.

### Co-Processing of Coal with Commingled Waste Plastic

Co-processing runs of Blind Canyon DECS-6 coal with commingled waste plastic (in a 1:1 ratio) involved adding several selected catalysts. Samples were subjected to the same temperature history at a hydrogen pressure of 900 psig. Figure 7 illustrates the TG weight loss curves of the coal, the waste plastic as well as the coal plastic mixture under non-catalytic conditions. The dotted line is the predicted weight loss curve of the mixture which is the linear sum of the individual component curves. The mixture of coal with waste plastic shows a slightly

lower reaction rate than the predicted value at 420 C. Subsequently, catalysts found effective in promoting the decomposition reactions of waste plastic including  $\text{ZrO}_2/\text{SO}_4^{2-}$ ,  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ,  $\text{NiMo}/\text{Al}_2\text{O}_3$  mixed with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and HZSM-5 Zeolite were applied to the mixture of coal with plastic. The TG weight loss curves presented in Figure 8 indicate that catalytic co-processing of coal with plastic is more difficult than catalytic processing of commingled waste plastic alone. The solid superacid catalyst  $\text{ZrO}_2/\text{SO}_4^{2-}$  and the cracking catalyst  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (added at the 10% level) have little influence upon the decomposition reactions of the mixture. A possible explanation could be that the presence of coal-derived nitrogen compounds poisons the active sites of the acid catalysts. By adding relatively large amounts (50%) of the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  catalyst, the decomposition rate is increased, but to a lesser degree than for waste plastic alone. The HZSM-5 catalyst shows a very promising result for co-processing of coal and waste plastic by increasing both reaction rate and volatile product yield. This confirms earlier results by Huffman and co-workers<sup>4</sup>. Apparently, the active sites of the HZSM-5 catalyst are much less readily poisoned by the coal compared to other catalysts. On the other hand, a mixture of  $\text{NiMo}/\text{Al}_2\text{O}_3$  with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  reveals better activity than the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  catalyst, whereas the opposite is true for plastic alone.

## CONCLUSIONS

High pressure TG/GC/MS is demonstrated to be a viable and useful technique for screening candidate catalysts for processing waste plastic and for co-processing coal with waste plastic.

At the high catalyst levels used the results reveal catalytic waste plastic cracking activity in the following order:  $\text{SiO}_2/\text{Al}_2\text{O}_3 > \text{HZSM-5} > \text{NiMo}/\text{Al}_2\text{O}_3$  mixed with  $\text{SiO}_2/\text{Al}_2\text{O}_3 > \text{solid superacids}$ . Of the solid superacids studied, the  $\text{ZrO}_2/\text{SO}_4^{2-}$  catalyst possesses the highest cracking activity and the approximate order of cracking activity is  $\text{ZrO}_2/\text{SO}_4^{2-} > \text{Al}_2\text{O}_3/\text{SO}_4^{2-} > \text{Pt}/\text{Al}_2\text{O}_3/\text{SO}_4^{2-} > \text{Fe}_2\text{O}_3/\text{SO}_4^{2-} > \text{no catalysts}$ .

The HZSM-5 zeolite catalyst shows most promising results for co-processing of coal with commingled waste plastic by increasing greatly the rate of the decomposition reactions albeit at the cost of lower MW products (high gas yields) and higher aromatic yields. Hydrocracking catalysts such as  $\text{NiMo}/\text{Al}_2\text{O}_3$  mixed with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  show potential promise for co-processing of coal with commingled waste plastic due to their hydrogenation and cracking ability.

## ACKNOWLEDGEMENTS

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Table 1  
Weight Loss Data from High Pressure TG

Items	Weight Loss, %
He	55%
H <sub>2</sub>	59%
Fe <sub>2</sub> O <sub>3</sub> /SO <sub>4</sub> <sup>2-</sup> , 10%	75%
Pt/Al <sub>2</sub> O <sub>3</sub> /SO <sub>4</sub> <sup>2-</sup> , 10%	79%
Al <sub>2</sub> O <sub>3</sub> /SO <sub>4</sub> <sup>2-</sup> , 10%	83%
ZrO <sub>2</sub> /SO <sub>4</sub> <sup>2-</sup> , 10%	86%
NiMo/Al <sub>2</sub> O <sub>3</sub> , mixed with SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> , 50%	97%
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> , 50%	94%
HZSM-5, 10%	97%

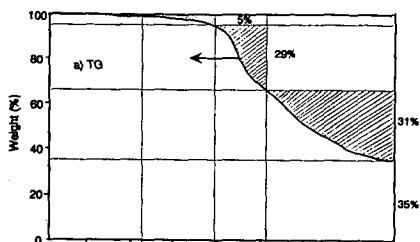


Figure 1. Hydropyrolysis of Blind Canyon DECS-6 coal. a) TG weight loss curve, b) total ion chromatogram.

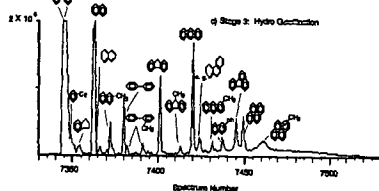
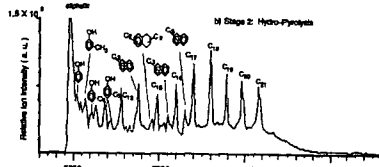
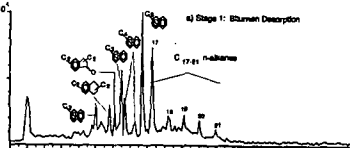
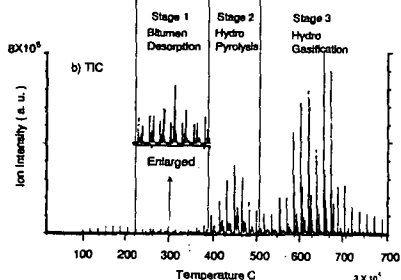


Figure 2. Product distribution obtained during hydropyrolysis of Blind Canyon DECS-6 coal. a) first stage-bitumen desorption; b) second stage - hydro-pyrolysis; and c) third stage - hydrogasification.

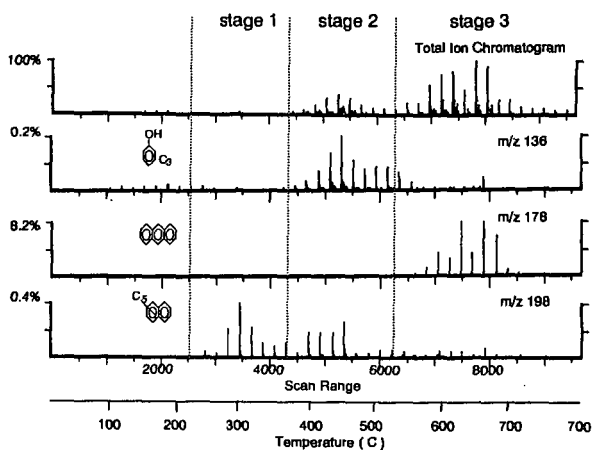


Figure 3. Evolution profiles of several products during hydrolysis of Blind Canyon DECS-6 coal by selective ion chromatograms.

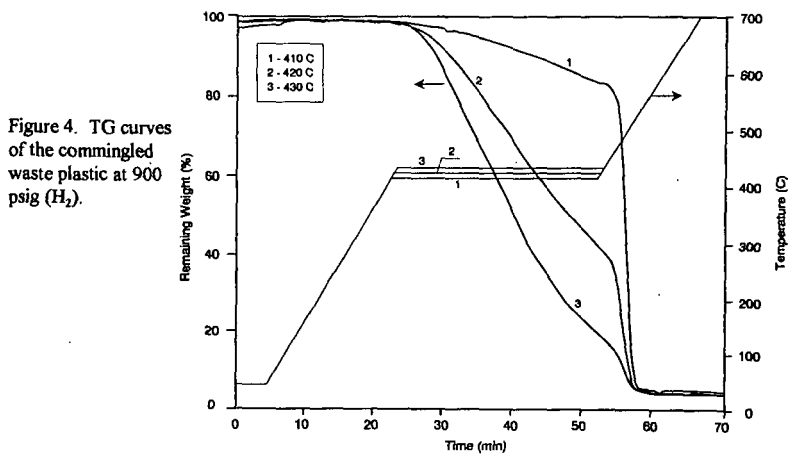


Figure 4. TG curves of the commingled waste plastic at 900 psig ( $H_2$ ).

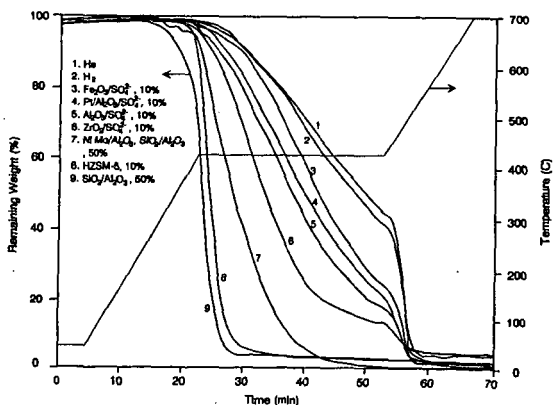


Figure 5. Effects of reactor gas atmospheres and catalysts on decomposition reactions of the commingled waste plastic at 900 psig.

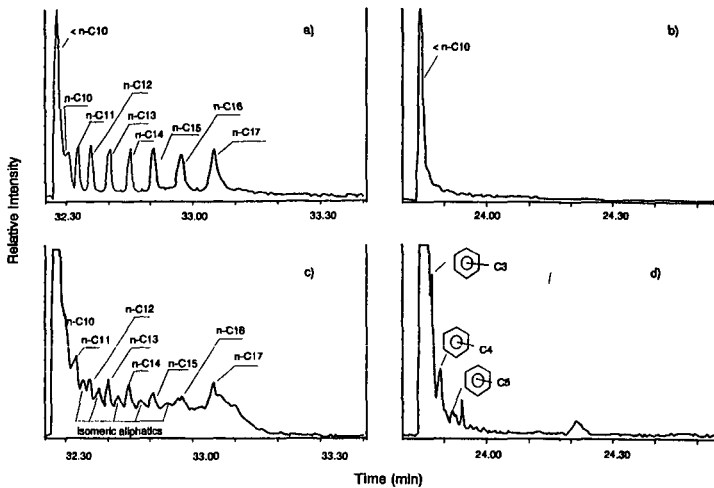


Figure 6. Total ion chromatograms of one sampling period of plastic decomposition products. a) in hydrogen; b)  $\text{SiO}_2\text{Al}_2\text{O}_3$ ; c)  $\text{ZrO}_2/\text{SO}_4^{2-}$ ; and d) HZSM-5.

Figure 7. TG curves of co-processing of coal with plastic at 900 psig ( $\text{H}_2$ ).

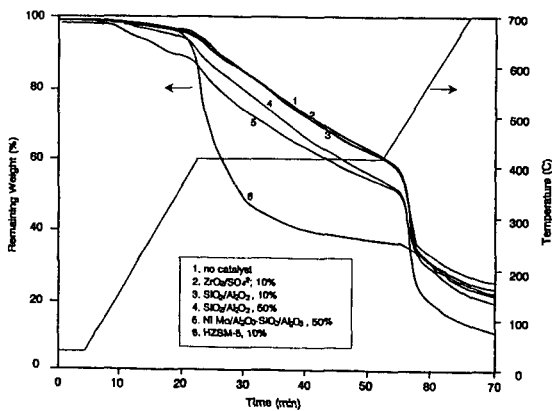
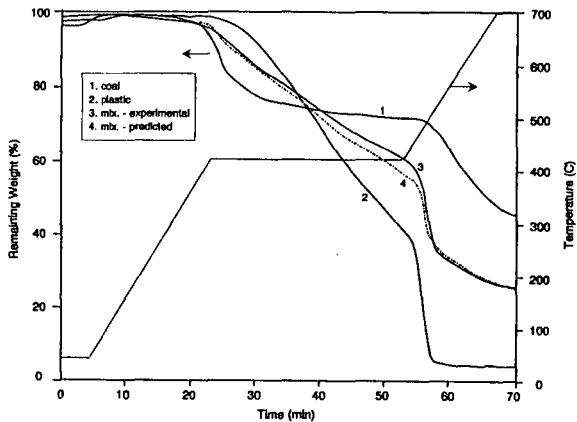


Figure 8. Effects of catalysts on co-processing of coal with plastic at 900 psig ( $\text{H}_2$ ).